Sulfur Removal from Reformate

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Even with the Proposed FY2004 Limit for Sulfur in Gasoline, Sulfur will still be Problematic

- New regulations will lower sulfur content in gasoline to 30-80 ppm from the current national average of 350 ppm (maximum of 1000 ppm).
- Autothermal reformate produced from these low sulfur gasolines will still contain 3-8 ppm of H_2S.
- H_2S at a concentration of 1 ppm has been shown to irreversibly poison the fuel cell anode catalyst.
- Sulfur and H_2S at these concentrations may poison fuel processing catalysts (e.g. reforming, water-gas shift, PROX)

Strategy

- As the sulfur content of gasoline decreases, the strategy for removing sulfur must change.
  - Sulfur removal technologies that can be used with current gasoline (avg. 350 ppm S) may be ineffective with future gasoline (30-80 ppm S).
  - Fuel processing catalysts may be able to tolerate the sulfur levels in reformate produced from low-sulfur gasoline.
- Near-term strategy - Adapt proven technologies capable of reducing H_2S to < 1ppm to fuel processing.
- Long-term strategy - Develop new technologies or improve existing technologies to meet the required H_2S levels.

Objective

- Develop a sulfur removal process that reduces the H_2S concentration to <1 ppm in reformate under fuel processing conditions:
  - H_2 and H_2O concentrations as high as 40% volume.
  - Temperature ranging from 80-800^{o}C.
- Compatible with design and operation of the fuel processor
  - Simple, requiring minimal processing and process control.
  - Maximum sulfur removal with minimal impact on weight/volume.
  - No unwanted byproducts requiring additional processing.

Approach

- Modeling
  - Identify parameters governing sorbent performance.
  - Predict sorbent lifetime and transient response.
- Synthesis/Fabrication
  - Develop coating processes for monoliths.
  - Develop new structured forms of ZnO.
- Experimental
  - Measure fundamental design parameters (sulfur loading capacity, reaction rates).
  - Evaluate sorbent performance in a microreactor system.
- Identify/Resolve Issues

Accomplishments and Activities During FY2000

- Developed a design model to predict performance of metal oxide adsorption bed.
- Concluded that a structured form of ZnO would be more effective than pellet form.
- Developed fabrication processes for producing new structured forms of ZnO.
- Experimental work to measure design parameters and to evaluate the sulfur removal efficiencies of new structured ZnO forms.

Reviewers’ Comments from FY1999 Annual Review

- Consider other developmental sulfur removal catalysts/technologies.
- Broaden the scope to include sulfur removal before autothermal reformer/POX.
- Bring in Materials group to develop a new sulfur scrubber.

We Considered Alternative Technologies, but still Conclude that Adsorption is the Most Effective

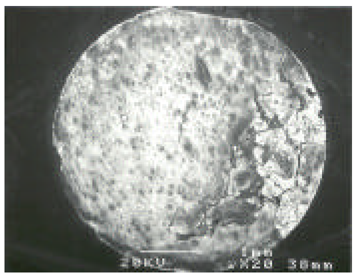
- On-board Pre-Reforming
  - Physical adsorption of organic sulfur compounds
  - Chemical reaction followed by sulfur removal
- Autothermal Reactor
  - Sulfur “getter” (similar to catalytic converter)
- CO Cleanup
  - Chemical adsorption with chemical reactivity
  - Physical adsorption/absorption of H_2S

Why Adsorption Technology? Why ZnO?

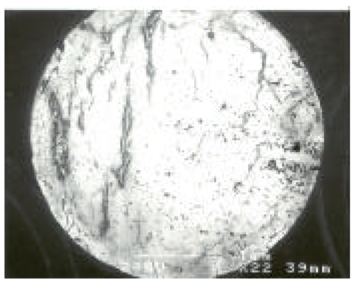
- Why Adsorption technology?
  - Advantage
    - Simple, easily integrated into current fuel processor designs
  - Disadvantage
    - Difficult to deal with sulfur in POX (unfavorable equilibrium/startup)
- Why ZnO?
  - Advantages
    - Favorable H_2S equilibrium at temperatures below <400°C.
    - ZnO is chemically stable under oxidizing/reducing conditions.
    - Does not promote unwanted side reactions.
  - Disadvantage
    - Slow intrinsic kinetics compared to oxides of Mn, Fe, Cu.

Exposure of ZnO Pellets to Fuel Processing Conditions Indicate Some Potential Problems

- Cracking and spallation are observed that can lead to bed blockage.

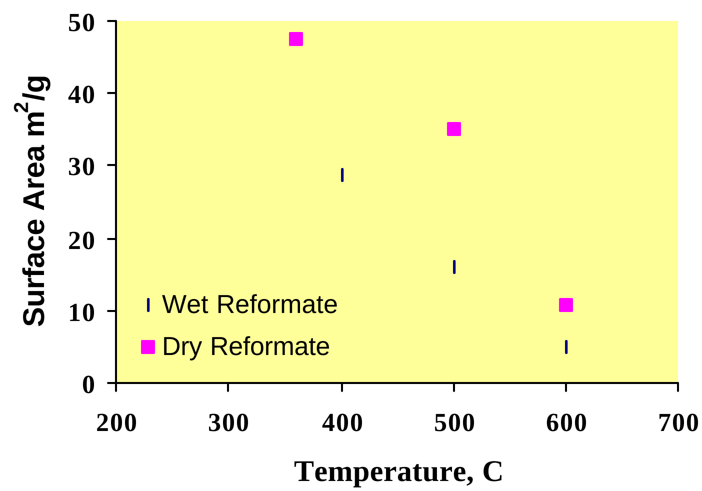


Commercial ZnO pellet exposed to 980 ppm H_2S in dry reformate at 400°C.



Commercial ZnO pellet exposed to 980 ppm H_2S in wet reformate (25% H_2O) at 400°C.

- Rapid loss of surface area if exposed to temperatures > 400°C will reduce H_2S uptake.



Commercial ZnO pellets exposed to dry or wet reformate (25% H_2O).

Pellet Form of ZnO is not Appropriate for Automotive Applications

- Commercial pellet form of ZnO is optimized for stationary applications.
  - Designed for high sulfur loading.
  - Normally operated at low H_2O concentrations (a few percent).
  - Not subject to rapid startup/shutdown.
- Potential issues for automotive applications.
  - Not designed for high space velocities (limited to < 2000 hr^{-1} at 10 ppm).
  - Vibrations could cause grinding resulting in bed blockage and significant back pressures.
  - Rapid startup can cause spallation resulting from water boiling in pore space.

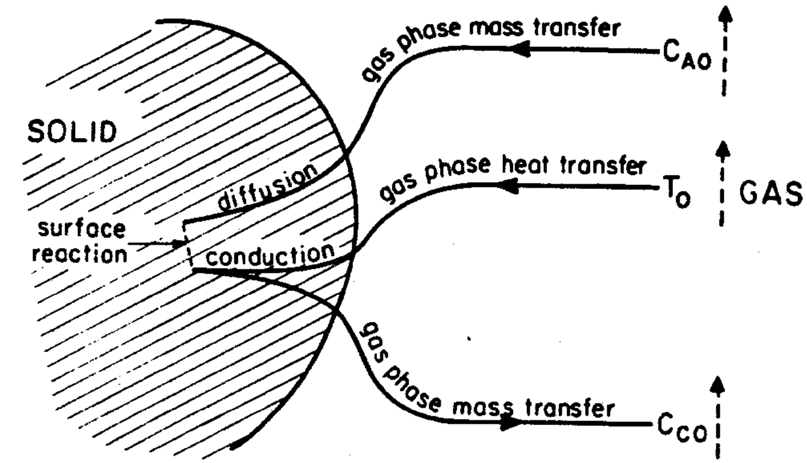
Structured forms of ZnO Better Suited for Automotive Applications

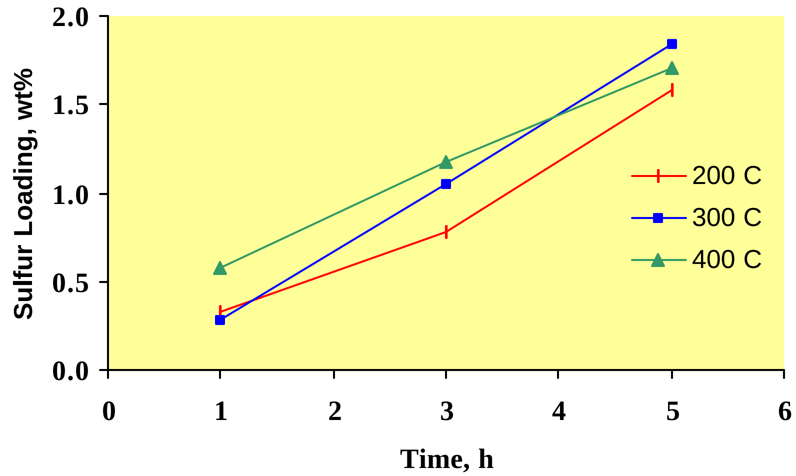
- Monoliths are an accepted technology in the automotive industry, used in the catalytic converter to minimize pressure drop.
- Monoliths and other structured forms have a higher surface-to-volume ratio than pellets which improve the sulfur removal rate.
- Uniformity of flow channels provides a more even flow distribution with a lower occurrences of channeling.
- Structured form of ZnO can significantly reduce the weight/volume of the sorbent unit given the low sulfur content of gasoline and the expected lifetime of the fuel processor.

Thin ZnO Layer Coating (50-100 :m) is Ideal for Optimizing Sulfur Removal

- Three fundamental processes that can determine the sulfur removal rate
  - External Mass Transfer
  - Diffusion
  - Reaction Kinetics

- For ZnO in pellet form
  - At low sulfur loading (<~2 wt% S), the sulfur removal rate is determined by the reaction kinetics.
  - As the ZnS product layer develops, the sulfur removal rate becomes diffusion controlled.
  - The ZnS product layer is ~75 :m thick at 1.5 wt%.





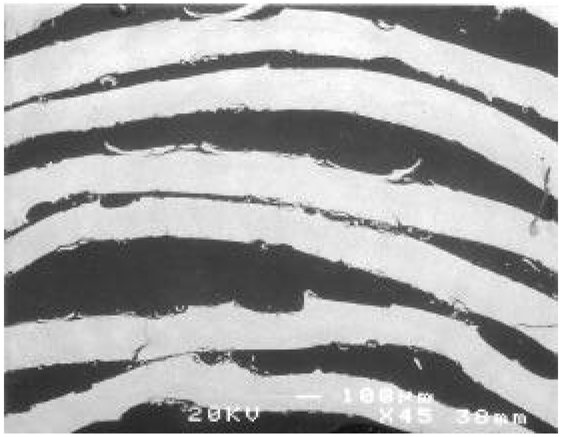
We have Developed a Process for Coating ZnO onto a Monolith

- A slurry-coating process is used to coat cordierite monoliths.
  - 20-40 wt% ZnO loading
  - Target is 50-100 :m ZnO layer

- We are having a major U.S. catalyst manufacturer produce ZnO-coated monoliths for testing.

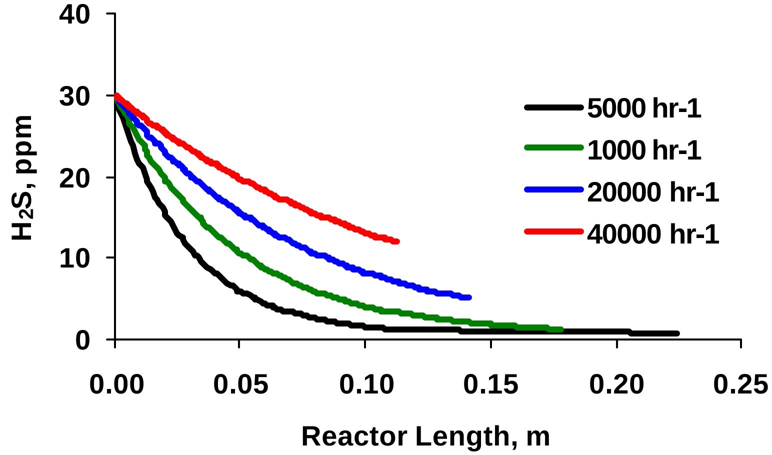
We have Developed A Process to Fabricate a Self-Supporting Form of ZnO

- Tape casting method to produce a structured form of ZnO.
  - 100 wt% ZnO
  - Uniform ZnO layer thickness
  - Self-supporting
  - Easily shaped
- In preliminary studies, able to reduced H_2S from 30 ppm to <10 ppm at 8000 hr^{-1}.
- Investigate composite materials with superior mechanical strength that can be easily form into any desired shape.

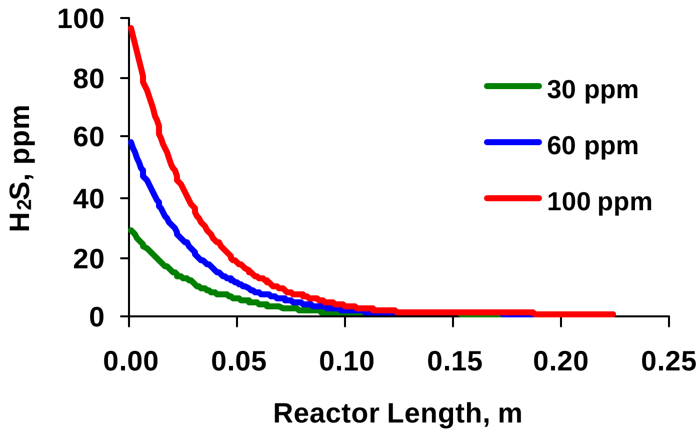


Using Modeling, We can Predict the Performance of Structured ZnO Forms

- Modeling is used to optimize the bed design as well as predict responses to transients.



Response of a ZnO-coated Monolith designed for 20 kWe operating at 50 kWe as a function of design space velocity



Response of a ZnO-coated Monolith designed for 20 kWe operating at 50 kWe Operation as a function of H_2S concentration.

- Based on modeling, we estimate that using a ZnO-coated monolith will reduce the bed weight by ~75% compared to ZnO pellets.

Future Work

- Evaluate the performance of commercially produced ZnO-coated monoliths with sulfur-containing fuels to reduce H_2S to < 1 ppm.
- Develop structured forms of ZnO using composite materials to improve reactivity and mechanical properties.
- Investigate the sulfur tolerance of fuel processing catalysts under processing conditions and the fate of sulfur during startup to better define the level of desulfurization required.
- Develop a adsorption process capable of reducing the H_2S concentration <0.1 ppm to protect the fuel cell anode catalyst but would not be integrated into the fuel processor.

Timelines/Milestones

FY98	5/99 - Initiated Project
FY99	1/99 - Completed construction of sulfur test reactor 2/99 - Established operating conditions for ZnO pellet bed 7/99 - Incorporated ZnO pellet bed into integrated fuel processor
FY00	11/99 - Concluded ZnO-coated monolith can significant reduce weight 1/00 - 4/00 Developed new structured forms of ZnO Summer 00 - Initiate testing of commercial ZnO-coated monolith
FY01	6/01 - Complete evaluation of commercial ZnO-coated monolith 9/01 - Complete evaluation of sulfur tolerance of fuel processing catalysts

GOAL

Develop a sulfur removal process to permit the use of gasoline with 30-80 ppm sulfur